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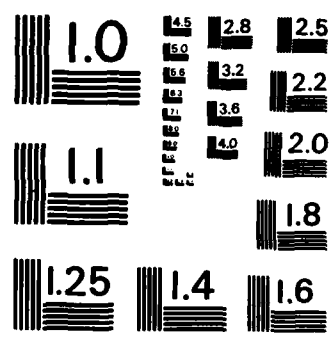
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Intramolecular Coupling in Metal-Free Binuclear Phthalocyanines

BY

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Intramolecular Coupling in Metal-Free Binuclear Phthalocyanines

By Elaine S. Dodsworth, A.B.P. Lever*, Penny Seymour and C.C. Leznoff

Abstract

The electronic absorption and emission spectra of a series of mononuclear and binuclear metal-free phthalocyanine species are reported. The binuclear species are linked through a benzene ring by a bridge of 0, 1, 2, 4 or 5 atoms. The spectroscopic data for the binuclear species, are analysed in terms of exciton coupling between the two halves of the molecule. Intramolecular coupling is seen to depend upon the nature of the bridging link. In some cases a cofacial conformation is possible; this gives rise to characteristic long-lived emission near 750nm.

Aggregation is a well known phenomenon in phthalocyanine chemistry.¹⁻³ Interactions can occur between adjacent phthalocyanine rings both in organic and aqueous phase, resulting in coupling between the electronic states of two, or more, phthalocyanine units. Recently we reported binuclear phthalocyanines⁴⁻⁶ involving phthalocyanine units linked through a benzene ring by bridges of 5^{4,5} and 2 and 4⁶ atoms, and we wish to probe the degree of intramolecular aggregation and the extent of electronic coupling between the two halves of the binuclear molecule. Such coupling is of interest, for

example, in the context of the design of multi-electron redox catalysts for electrocatalytic and photocatalytic processes, and for studies of energy transfer in biological systems.

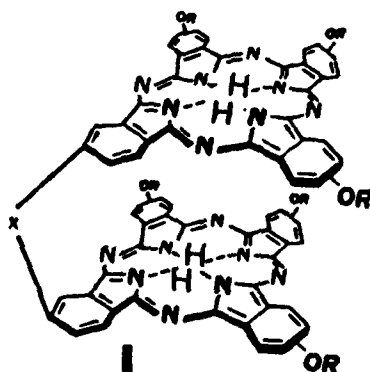
Some of the binuclear species described here appear capable of closing in a 'clamshell'-like fashion and a spectroscopic probe of this possibility is desirable. Of relevance to this communication are species involving two phthalocyanine units linked via a benzene ring (3 or 4 position) (I) in the following fashion.

Label

- Pc-Pc(0) Directly linked phthalocyanine rings.
O(1) Phthalocyanine rings linked via an oxygen atom.
C(2) Phthalocyanine rings linked via $-\text{CH}_2-\text{CH}_2-$.
C(4) Phthalocyanine rings linked via $-(\text{CH}_2)_4-$.
Cat(4) Phthalocyanine rings linked via o-catecholate, $\text{Pc}-(\text{cat})-\text{Pc}$.
t-BuCat(4) Phthalocyanine rings linked via 4-t-butyl-o-catecholate.
EtMeO(5) Phthalocyanine rings linked via $-\text{OCH}_2\text{C}(\text{Me})(\text{Et})\text{CH}_2\text{O}-$

The number in parenthesis is the number of atoms (0-5) in the bridge link. The phthalocyanine units have neopentoxy groups substituted onto each of the three remaining unlinked benzene rings, conferring relatively high solubility in organic solvents. The neopentoxy groups randomly distribute in the 3 or 4 positions. The presence of these isomers (which are very difficult to separate) precludes formation of good crystals and hence X-ray analysis of these systems.

These species may exist in various conformations. Some, e.g. EtMeO(5), may exist in a cofacial or closed 'clamshell' configuration and may be thought to 'open' or 'close' by rotation about the bridge.⁴ For others, such as Pc-Pc(0), an intramolecular cofacial conformation is obviously



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impossible.

Coupling between the two halves of the binuclear molecule may occur through mechanisms described below. In this paper the degree of coupling is explored as a function of the nature of the bridge and of temperature.

'Clamshell' and cofacial porphyrins have been studied extensively.⁷⁻¹² There is a major difference between porphyrins and phthalocyanines in that there is significantly greater intensity in the Q band region of the electronic spectra of the latter, relative to the former, and therefore a larger transition moment. Interactions which are indicated by broadening of the Soret region or small shifts in the Q band region, in the porphyrin series, are readily observable as a much more dramatic effect on the Q band region of the phthalocyanines.

Experimental

Electronic absorption spectra were recorded with a Perkin Elmer-Hitachi Model 340 microprocessor spectrometer. Emission and excitation spectra were recorded with a Varian SF330 spectrofluorimeter with appropriate filters to eliminate problems associated with light at twice the exciting wavelength. Low temperature absorption and emission spectra utilised a Beckman Variable Temperature cell with quartz windows. Emission lifetimes were obtained using a York University-constructed nitrogen pulsed laser, a PARC model 162 Boxcar mainframe with ratio card and model 165 and 166 gated integrators. The signal was fed to a R928 photomultiplier using an appropriate interference filter.

Toluene was Aldrich Gold Label, and ethanol (100%) was distilled from sodium under nitrogen. The various phthalocyanine species were prepared and purified by literature routes.⁴⁻⁶ The synthesis and characterisation of the (here, newly described) Pc-Pc(0) and Pc-O-Pc, O(1), binuclear species will

be reported elsewhere.

The solid state spectra were obtained by grinding a sample and then smearing on a quartz plate. The Nujol mull spectra were obtained by mulling as for an infrared spectrum.

Results and Discussion

The electronic absorption spectrum of a phthalocyanine species can provide a sensitive probe for the presence or absence of coupling between two (or more) phthalocyanine units. In the absence of coupling, the D_{2h} symmetry, metal-free phthalocyanine shows two strong sharp bands in the 650-720nm region, plus two weaker vibrational components to higher energy of the main absorption.¹³ An example of such a spectrum for a mononuclear metal-free phthalocyanine is shown in Fig.1A. Such a mononuclear species generally shows no sign of intermolecular aggregation in common organic solvents at concentrations below $1 \times 10^{-5}M$ at room temperature. At higher concentrations, however, intermolecular aggregation can occur.^{3,14}

The spectroscopic signature of a binuclear phthalocyanine is determined by the extent of coupling. A fully uncoupled species will display an electronic spectrum apparently identical to that of its mononuclear analogue, as Fig.1A, in this case. Coupling may, in general, be expected to occur i) through space in a closed cofacial 'clamshell', ii) through space between two halves of a binuclear molecule in a partially 'open' or fully 'open' conformation, or iii) via conjugation through an unsaturated bridge.

Further we anticipate that these binuclear species exist in dynamic equilibrium between the various conformations, depending upon the nature of the bridge. In some cases steric effects may provide barriers to free rotation. However a solution at room temperature is likely to contain a selection of species from strongly coupled to uncoupled and the electronic

absorption spectrum will be a composite of the absorption spectra of these species.

These binuclear metal-free phthalocyanines show broad and moderately intense absorption in the 610-650nm region with weaker peaks on a broad background in the 650-720nm region (Fig.1B-H), the latter corresponding to the mononuclear absorption (Fig.1A). The shift of absorption intensity to higher energy, relative to the mononuclear species, is a direct indication of coupling¹⁵, and the broadness may reflect the diversity of conformers in solution. Moreover such spectra are observed essentially unchanged down to $5 \times 10^{-7}M$, indicating that the coupling is intramolecular in nature.

In view of the dynamic nature of the equilibrium, it is not useful to try and establish an intra-phthalocyanine separation. However it is feasible to use absorption and emission spectra to ascertain an approximate idea of the degree of coupling, and how this varies with temperature and bridging link. Such information is useful to obtain a clearer picture of the physical chemistry of the binuclear species, and hence facilitate design of useful catalysts. Note that there is some solvent dependence in the electronic spectra, usually reflected in variations in relative peak intensities.¹⁶ These effects are not covered here.

i) Theory of intraphthalocyanine coupling - qualitative

The intense absorption in the visible region, the Q band, results from the $a_{1u} \rightarrow e_g$, $\pi \rightarrow \pi^*$ transition, generating an orbitally doubly degenerate state in metal phthalocyanines of D_{4h} symmetry. In the free base, the symmetry is lowered to D_{2h} and the excited state is split into two components usually termed Q_y and Q_x . These then are the two principal 650-720nm region absorptions in the mononuclear species. The two weaker absorptions are vibrational (1-0) overtones of Q_y and Q_x . The accepted coordinate frame requires $E(Q_x) < E(Q_y)$.^{16-18a}

The theory of interaction between phthalocyanine and between porphyrin molecules has been discussed in the literature^{15,18-23} especially in the context of cofacial diporphyrins and chlorophyll dimers^{7-12,24,25} aggregated porphyrins^{26,27} and oxo-bridged porphyrins,¹⁹ and is generally based on exciton coupling^{19,28,29}.

The exciton coupling model is a state interaction theory. The transition moments in the two excited states Q_x , Q_y couple, in and out-of-phase, between the two halves of the binuclear species. The coupling is proportional to the magnitudes of the transition moments and inversely proportional to the cube of their separation. In D_{4h} symmetry, two pairs of doubly degenerate states will then arise, with transitions to the two upper, in-phase coupled states allowed (these will be blue shifted relative to the mononuclear case), and transitions to the lower out-of-phase combinations being forbidden.³⁰ In the D_{2h} symmetry of the metal-free derivatives, the Q_x and Q_y states will split and the coupling will result in a pair of non-degenerate in-phase higher energy combinations (Q_{y+}, Q_{x+}) and a pair of lower energy out-of-phase combinations (Q_{y-}, Q_{x-}) (Fig.2).

In this exciton model the ground state of the binuclear system corresponds with that of the mononuclear unit but may be stabilised by van der Waals's interaction energy. It is not split.

Alternatively, molecular orbital theory may be utilised, for example, in the 'four orbital model' in which the ground state HOMO and excited state LUMO on each component of the binuclear species couple in and out-of-phase. The levels so generated will produce an energy level diagram rather like that shown in Fig.2 but the physical significance is quite different.²⁴ The molecular orbital model does provide for possible interaction between the HOMO levels of each half of the molecule, resulting in a non-degenerate pair of levels.

In the low symmetry of the real binuclear molecules (tilted and slipped conformations etc), transitions to both the higher and the lower energy combinations can be expected, yielding intensity both blue and red shifted with respect to the mononuclear case.¹⁹ A range of energies is anticipated for the in-phase and out-of-phase combinations, arising from the various conformations. At room temperature a Franck-Condon electronic excitation will see a summation of all the dynamic conformations which exist in solution. Without discussing the added complexities of solvent effects varying from mononuclear to binuclear species, a broad absorption is predicted, shifted to the blue of the mononuclear absorption and possessing a broad weak tail to the red. Superimposed on this envelope will be the two Q peaks of species in which the two halves of the molecule are sufficiently uncoupled to be regarded simply as two independent mononuclear species tied together. This overall appearance is in fact observed for all the binuclear species studied (Fig.1B-H), but with a pair of peaks observed rather prominently to the blue of the mononuclear absorption.

The Soret region (300-450nm) ($a_{2u} \rightarrow e_g, \pi \rightarrow \pi^*$) shows a prominent peak near 350nm and a well defined shoulder near 400nm (Fig.1B-H). This shoulder does not arise from exciton splitting since it is also present in PcH_2 (Fig.1A). However there is a definite blue shift in the Soret peak in the binuclear species compared with the mononuclear.

The intensity of the 650 - 720nm peaks relative to those in the 600-650nm region reflects, qualitatively, the extent of coupling of the binuclear species. This is seen to vary dramatically through the series, and to be a minimum with the catechol based species. We return to this variation in the emission discussion below.

ii) Low temperature absorption spectra (Toluene/Ethanol)

Cooling a solution to a glass at liquid nitrogen temperature causes marked changes in the spectra (Fig.1). In all cases, absorption between 600 and 650nm becomes more intense relative to absorption in the 650 - 720nm region, where the peaks become less prominent. This is believed to be associated with a greater degree of coupled character at lower temperatures, as previously seen with the cobalt derivatives⁴.

The range of conformations which must exist dynamically in a fluid solution will freeze out, probably to several preferred, and evidently more completely coupled, conformations, at liquid nitrogen temperature. The simplest binuclear species is Pc-Pc(0) whose low temperature spectrum exhibits more coupled behaviour than the room temperature spectrum. It is likely that the two phthalocyanine units rotate around the C-C bond at room temperature but are frozen out at liquid nitrogen temperature, perhaps to a co-planar arrangement, though this may be inhibited by steric interactions between hydrogen atoms on the two linking benzene rings. Entropy considerations should also favor fewer conformations at cryogenic temperatures.^{27,31} Intermolecular aggregation is also likely to become more important, and such aggregation may favour a more parallel arrangement of phthalocyanine rings. Only such intermolecular aggregation is possible for the mononuclear species.

The two peaks near 610 and 640nm vary in their relative intensity in the several binuclear species, probably as a consequence of variations in the preferred low temperature conformations. However, at this time it is not possible to be more specific.

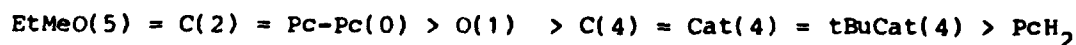
iii) Room temperature emission spectra (Toluene/Ethanol)

The mononuclear species emits strongly at 709nm, fluorescing from the Q band states^{18b,23,32,33} with a very small Stokes shift (Fig.3). Much

weaker shoulders near 735 and 775nm are vibrational structure. When a sample is cooled to liquid nitrogen temperature, only weak emission is observed at 696nm (Fig.3, Table 1). The excitation spectra of this 709nm (or low temperature 696nm) feature, or its vibrational satellites, are the same as the absorption spectrum in the Q band region (see Fig.4B for excitation spectrum of a vibrational satellite at low temperature).

The binuclear species also exhibit a band near 710nm at room temperature in solution, but it is much weaker in emission intensity than in the mononuclear species. Vibrational satellites appear in the same positions as in the mononuclear spectrum. The weaker intensity probably reflects intramolecular self-quenching between the coupled halves of the binuclear species through several possible mechanisms including relaxation to triplet states²⁹ and non-radiative vibrational relaxation³¹ (Fig.3). The excitation spectra of the 710nm binuclear emission, and its vibrational satellites, are similar to the absorption spectrum of the mononuclear species with maxima between 650 - 720nm and relatively weaker excitation in the 600 - 650nm region (Table 2).

The degree of self-quenching may be calculated from the intensity of the ca.710nm emission in the binuclear species relative to that of the mononuclear case. These data (Table 3) may roughly reflect the degree of uncoupled conformer in each species at room temperature. The extent of coupling decreases in the sequence:-



which sequence also approximately parallels the ratio of the peak intensities of the 610-650nm absorption relative to that at 670-710nm. This sequence depends, somewhat, upon the nature of the mixture of substituent isomers obtained for each species, a subject to which we return below.

iv) Low temperature emission spectra (Toluene/Ethanol)

When cooled to liquid nitrogen temperature, binuclear species show a marked reduction in emission intensity in the 700nm band, and a shift of about 10nm to shorter wavelength. The reduction in intensity is consistent with the increased coupling at the lower temperature since relaxation will become more efficient.

Three binuclear species, EtMeO(5), Cat(4) and t-BuCat(4) show an additional emission band near 750nm which appears in the frozen glass but not in the liquid solution. This emission peak is not observed in the low temperature glass spectra of the other binuclear species (Fig.3). We propose that the 750nm emission originates in the coupled conformers. The excitation spectra of the 750nm band in these three binuclear species also show peaks in the 650 - 720nm region but the excitation in the 600 - 650nm region is relatively significantly greater than for the 700nm emission. Moreover there is a pronounced excitation peak near 720nm which is only weakly evident in the absorption spectra (Fig.4D, Table 2). This may be due to direct excitation to an out-of-phase coupled excited state (Q_{y-}) with a high efficiency of relaxation to Q_{x-} .

This behaviour parallels, for example, that observed for monomeric and dimeric chlorophyll derivatives, in that the excitation spectra of monomeric and dimeric species are different³⁴, and earlier work where excitation spectra discriminated between the origins of emission of dimeric porphyrins^{10,11} (see further development below). Certain monomeric zinc porphyrins also show emission from dimeric forms generated in low temperature solution.²⁷

The presence of excitation for the 750nm emission occurring in the 670 - 720nm region, and specifically the peaks therein, implies a mechanism which permits excitation of the uncoupled species to generate emission from

the coupled species.^{11,34} Energy transfer may be occurring from an excited uncoupled conformer to lower energy states in the coupled species.

v) Deprotonated binuclear metal-free phthalocyanine spectra

The addition of 0.1-0.2ml of tetrabutylammonium hydroxide (1M in MeOH) to solutions (ca 5×10^{-6} M) of metal-free binuclear species in a cuvette, provides a rapid means of obtaining the electronic spectra of the deprotonated species. These are also presented in Fig.1A-H, and Table 4. Deprotonation raises the symmetry of an individual phthalocyanine unit to D_{4h} so that the double Q band should collapse, in the absence of coupling, to a single strong Q band plus its vibrational partner.²³ This is observed for the mononuclear and C(4) species, which show a single peak centred near 680nm (Fig.1A,G). However the remaining binuclear species show two distinct types of behaviour.

In one group we observe a structured Q band centred at 680nm, obviously a doublet but with closer spacing than the protonated species (Fig.1B,C), while the other group (Fig.1D,E,F,H) shows prominent absorption near 645nm, in some cases also associated with 680nm absorption (Fig.1D,F). As discussed below, these data add considerable insight into the nature of the coupling in these binuclear species.

vi) Binuclear conformations

It is useful to summarise the above data and subdivide the various spectra into groups of observations:-

- a) Only the EtMeO(5), Cat(4) and t-BuCat(4) species show the 750nm emission.
- b) Only the EtMeO(5), Cat(4) and t-BuCat(4) deprotonated species show the 645nm absorption peak as the strongest band.
- c) Only the EtMeO(5), Cat(4) and t-BuCat(4) species have the capability of forming a cofacial or approximately cofacial conformation. The others,

except perhaps for C(4), are precluded by the configuration of the bridge from becoming cofacial.

d) Only the mononuclear and C(4) deprotonated species show a single 680nm absorption.

e) Only the Pc-Pc(0) and O(1) deprotonated species show a doubled Q band near 680nm.

f) The two catechol bridged deprotonated species show both the 640 and 680nm absorption.

The existence of 610 - 650nm absorption in the O(1) and Pc-Pc(0) binuclear species, and especially the presence of the obviously exciton-split Q band in the deprotonated versions of these species, clearly establishes through-space coupling between the halves of these binuclear species which cannot be cofacial.

Exciton coupling occurs between transition moments on each phthalocyanine ring through the space between the two halves (or via conjugation in the case of Pc-Pc(0)). The extent of coupling is proportional to the square of the monomer transition moment which is very large in the case of phthalocyanine Q band absorption. It is inversely proportional to the cube of the distance between the two halves of the molecule and is therefore effective over quite long distances.^{15,19,28,29} The bridge may be flexible such that there will be relative rotation of the two phthalocyanine halves. However there will always be orientations which do not negate coupling. All of the binuclear species show absorption in the 610 - 650nm region as a consequence of this through-space coupling, which does not require inter- or intramolecular aggregation.

The peaks in the 670 - 720nm region then reflect the contribution due to uncoupled or extended conformations with long distances between the two halves.

The special characteristics of the EtMeO(5), Cat(4) and t-BuCat(4) species are most readily explained in terms of cofacial intramolecular aggregation, a conclusion supported by construction of molecular models. This is reasonably responsible both for the 750nm emission, and for the shift to 640nm of the Q band of the deprotonated species. The cofacial conformer could be staggered (D_{4d}) or eclipsed (D_{2h}) subject to steric constraints by the bridge link; they are potentially distinguishable since the former has only one higher energy Q band transition while the latter has two.¹⁹ Both can have electronically allowed lower energy absorption to the O_y-O_x states. The extreme broadness of the electronic spectra does not permit us to draw any conclusions concerning this question.

Molecular models show that there may be more steric hindrance in the catechol bridged species, than in EtMeO(5). The multiple bands in the spectra of the deprotonated catechol-bridged species may then reflect an equilibrium between cofacial and non-cofacial conformations.

Note that the deprotonated species exhibiting 645nm absorption must be conformationally different from the other species, otherwise they would show 680nm absorption. This is most readily reconciled by the cofacial conformation. However it is surprising that two Pc^{2-} units would (intramolecularly) aggregate strongly. There is the possibility that the 640nm species is only partially deprotonated and that the remaining proton(s) acts to bind the two halves together by hydrogen bonding. However we have been unable to modify the spectrum by addition of further excess base, or by addition of a proton sponge.

The single 680nm band in the deprotonated mononuclear and C(4) binuclear species reveals that the C(4) species does not form a cofacial conformer to any detectable degree. The C(4) binuclear species also has a room temperature electronic spectrum similar to that of the mononuclear species.

The exciton model shown in Fig.2 is valid for both through-space non-cofacial and cofacial coupling. Thus one might question why the 750nm emission is only seen in the cofacial cases. We note that such emission is only seen weakly and at liquid nitrogen temperature when the cofacial conformation is maximised. It is possible that vibrational/rotational modes associated with the bridge of an 'open' non-cofacial, but coupled, species provide a pathway for non-radiative relaxation. This could also be a relaxation mechanism at room temperature for those species which show the 750nm emission at liquid nitrogen temperature. Further note that the intensity of the 750nm emission is very low (see Fig.3) there probably being energy transfer to the phthalocyanine spin-triplet state near 1000nm.^{9b,11,28,29,32} The cofacial excited states may also have a contribution from charge transfer states such as $P_a^-P_b^+ + P_a^+P_b^-$ which could provide a mechanism for radiationless decay.

It may be useful to view the emission in terms of the formation of an excimer. It is likely that the two halves of the cofacial conformer are more strongly bound in the excited state than in the ground state. Assuming the ground state is much less strongly bound, the emission should be red-shifted from the monomer emission and should be broad and structureless³¹ as is the case.

vii) Quantitative aspects of exciton coupling.

In the mononuclear control molecules the intense emission at ca. $14,100\text{ cm}^{-1}$ (709nm) corresponds to fluorescence from Q_x and is a (0'-0'') transition whose (1'-0'') and (2'-0'') satellites are observable (see Table 1). The splitting of approximately 750 cm^{-1} corresponds^{18b} with an intense and narrow feature in the infrared spectrum at 744.5 cm^{-1} , due to an aromatic C-H out-of-plane deformation. In centrosymmetric molecules, the vibrational emission must be g+g and therefore cannot be identified directly

with an observed infrared absorption band. However the ring substituents may weaken this selection rule.

Using Figs.1,2, the two peaks near 16,350 (610nm) and 15,625 cm^{-1} (640nm) in the binuclear derivatives are then the transitions to Q_{y+} and Q_{x+} respectively. Their separation is almost exactly the same as in the mononuclear species (14,925, 14,165 cm^{-1}).

The cofacial conformer emission at ca.13,250 cm^{-1} (750nm) almost certainly arises through emission from the lowest level, Q_{x-} . Since the Stokes shift is expected to be less than 100 cm^{-1} (cf. mononuclear absorption, 14,165 cm^{-1} and emission 14,105 cm^{-1}), this 13,250 cm^{-1} emission may be the ($0'-0''$) transition between Q_{x-} and the ground state. This should be relatively long lived since, at least in the higher symmetry conformers, emission therefrom is forbidden.²⁹

The excitation peak at ca.13,900 cm^{-1} is most reasonably assigned to a transition to Q_{y-} , which then relaxes to Q_{x-} with a high quantum yield.

With these assignments we obtain:-

$$E(Q_{y+}) - E(Q_{x+}) = \text{ca. } 840 \text{ cm}^{-1}$$

$$E(Q_{y-}) - E(Q_{x-}) = \text{ca. } 645$$

and two direct estimates of the exciton splitting:-

$$E(Q_{y+}) - E(Q_{y-}) = \text{ca. } 2450 \text{ cm}^{-1}$$

$$E(Q_{x+}) - E(Q_{x-}) = \text{ca. } 2255$$

This average value of 2350 cm^{-1} corresponds exactly with a LUMO-LUMO interaction splitting energy of 2400 cm^{-1} calculated for a cofacial PcSi-O-SiPc binuclear species.³⁵ It is significantly larger than observed in various porphyrin and chlorophyll systems.^{19, 36}

One might try to estimate the average cofacial intramolecular distance using the exciton model and the transition moment evaluated from the oscillator strength of the monomer unit.²⁸ Although this calculation does yield reasonable numbers, it is considered inaccurate when the intramolecular distance is small compared with the molecular dimensions.^{15, 37}

viii) Lifetimes

The ca 710nm emission is very shortlived, being allowed fluorescence (within lifetime of our laser <15ns). The ca 750nm emission of the low temperature cofacial samples originates from a 'forbidden' excited state and should therefore have a longer lifetime. Measurements with the sample cooled to 77 K reveal a lifetime for EtMeO(5) of ca 50ns. This is in keeping with the model developed here.

ix) Solid state absorption spectra

In order to gain some insight into the conformations which exist in the solid state, the electronic spectra were recorded as Nujol mulls, and as smears on a quartz plate (Fig.5, Table 5). There may be problems arising from scattering effects caused by differences in particle size etc. (sample preparation), but it is possible to make some generalisations.

In all cases, the Nujol mull spectra clearly resemble the spectra of the frozen solutions, though in some cases (PCH₂, Pc-Pc(0), O(1) and C(4)) the LT glass spectra appear to show more coupling than the mulls (more intensity to the blue). These substituted phthalocyanines do show some degree of solubility in Nujol. Possibly the mull should be regarded as a very viscous solution rather than a suspension of small particles.

The solid smear spectra of all the binuclear species show absorption red shifted from that in solution and from that of the mononuclear. Since

unsubstituted phthalocyanines show semi-conductor behaviour in the solid state²², the red shift may be due to the generation of band structure in the solid state, due to intermolecular stacking.

x) Complexities due to the presence of isomers

The mononuclear species PcH_2 exists as a mixture of four geometric isomers as a consequence of the distribution of the neopentoxo groups. There appear to be no significant electronic spectroscopic consequences in the sense that all the isomers probably have very similar spectra.

This is not quite true for the binuclear species, since the possible conformations of a specific molecule will be influenced by which of the possible 18 geometric isomers is concerned. In the case of $EtMeO(5)$, for example, the cofacial conformer is apparently not formed with equal ease by all geometric isomers. While we have not found it possible to separate these various geometric isomers, chromatography will yield fractions containing varying mixtures of isomers. The electronic absorption and emission spectra reported in this paper are for representative mixtures of isomers. The reader should be aware that their preparation may have a different mixture and give rise to somewhat different spectroscopic characteristics. The differences will be reflected in a different degree of 'average' coupling. We expect such differences to be fairly small except perhaps in the case of $EtMeO(5)$ where we have observed rather larger variations from one sample to another. Note finally that there is only one geometric isomer with respect to the bridging link, say 3,3- but that rotation of one phthalocyanine unit about the other will generate a 3,4- conformational isomer. If rotation is hindered, these two conformers may both be present and may have different spectra.

Summary and Conclusions: The EtMeO(5), Cat(4) and tBuCat(4) binuclears show equilibria between cofacial and non-cofacial conformations, with the first, at least in some of its isomers, having the highest proportion of cofacial. Pc-Pc(0) and O(1) are quite similar in behaviour, with no possibility for intramolecular cofacial arrangements, but showing significant inter-ring coupling. C(4) is largely uncoupled with little tendency to form cofacial conformers, and with a spectrum, under the various conditions, not very different from the mononuclear. This is rather surprising. Molecular models do not show any obvious reasons for this behaviour; it would appear sterically possible to form cofacial conformers. The C(2) species has behaviour intermediate between C(4) and O(1) as might be expected.

The electronic spectra of Co(I), Co(II) and Co(III) derivatives of most of these species have been recorded;³⁸ in general the degree of coupling between the two halves of the metallated species parallels the behaviour discussed here. Of considerable importance, is the observation of a rough correlation between the degree of electronic coupling between the two halves of the cobalt species, and the ability of the cobalt species to electrocatalytically reduce molecular oxygen. Future studies will extend to iron complexes and will seek to understand the mechanism causing this important correlation.

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30. The choice of phase is arbitrary depending upon a choice in the phase of the transition moment.²⁹ One state will be stabilised and one destabilised by the coupling. In the exciton model, the node corresponding to the negative sign is an excitation node, not an electron orbital node. It corresponds with a change in the phase relation between transition moments on each component of the binuclear species.
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Table 1 Absorption and Emission Electronic Spectroscopic Data for Mononuclear and Binuclear Metal-Free Phthalocyanine Species in Toluene/Ethanol (3:2 v/v).

Species	Temp.	Absorption Spectra (nm) ^a				Emission Spectra (nm) ^b		
		Log(ε)						

PcH ₂ ^c	RT	347(4.75)	(396)(4.52)	609(4.43)	645(4.64)	709		
		669(4.96) 707(5.03)						
	LT ^d	340s	(400)m	(612)s	634s 666m	696 735w 773w		
		702m						
Pc-Pc(0)	RT	334(4.90)	(390)(4.54)	640(4.72)	674(4.71)			
		700(4.66)						
	LT	(320)s	(400)s	625s				
O(1)	RT	335(4.97)	(390)(4.63)	(616)(4.79)	639(4.84)	707		
		669(4.81) 701(4.72)						
	LT		(400)s 632s	(668)s	(700)m	699 730w 772w		
C(2)	RT	339(4.45)	(390)(4.29)	621(4.34)	640(4.36)	706		
		666(4.38) 705(4.37)						
	LT			616s 640s 667m	700m	698 734w 776w		
C(4)	RT	338(4.84)	(390)(4.48)	(620)(4.62)				
		643(4.72) 673(4.77) 708(4.71)						
	LT	(320)s	(395)s	614s (640)s	672s			
		700s						
Cat(4)	RT	338(5.04)	(390)(4.71)	(618)(4.89)				
		640(4.95) 668(4.91) 704(4.80)						
	LT	610s	(670)w (700)w					
						697 751		

Table 1 cont-----

Species	Temp.	Absorption Spectra (nm) ^a Log(ϵ)	Emission Spectra (nm) ^b

tRuCat(4)	RT	337(4.87) (390)(4.52) 620(4.63) 644(4.72) 675(4.79) 710(4.80)	710 790w
	LT	613s (640)s 674s 708m	708 753 780w
EtMeO(5)	RT	331(4.93) (390)(4.52) (620)(4.65) 641(4.72) (673)(4.71) (708)(4.62)	709
	LT	612s (636)s (700)s	700 763

RT = Room temperature; LT = liquid nitrogen temperature glass.

a) Shoulders in parentheses. b) For corrected relative intensities, see Table 3. All emission peaks, except those shown in bold face, originate from the uncoupled conformer of the clamshell or mononuclear species. Bold face peaks originate from cofacially coupled clamshells, see text.

c) Tetraneopentoxypthalocyanine d) Relative intensities of glass spectrum indicated by s = strong, m = medium, w = weak. Absolute intensities are not reliable due to light scattering by glass.

Table 2 Excitation Electronic Spectroscopic Data for Mononuclear and Binuclear Metal-Free Phthalocyanine Species in Toluene/Ethanol (3:2 v/v)

Species	Fluorescent emission ^a	Temp.	Excitation Spectra (nm) ^a
PcH ₂ ^b	775 ^c	RT	610w 642w 671s 706s
	736 ^c	RT	609w 641w 671s 707s
	709	RT	612w 641sh 672s ^d
	697	LT	607w 640w 653vw 670s ^d
Pc-Pc(0)	705	RT	(627) (650) 678
	700	LT	615 648 679
O(1)	707	RT	614w 651w 674s ^d
	699	LT	607w 640w 652w 671s ^d
	733 ^c	LT	608w 640w 650w 671s 706s
	770 ^c	LT	614w 644w 671s 704vs
C(2)	706	RT	613w 644w 674s ^d
	698	LT	610w 642w 672vs ^d
C(4)	709	RT	614 (650) 676
	700	LT	612 648 674
Cat(4)	705	RT	611w 640w 673s ^d
	698	LT	610w 642w 650vw 672s ^d
	754 ^e	LT	617m 650m 674s 704m 718s
tBuCat(4)	710	RT	617w 645w 676s ^d
	709	LT	610w 650m 680s ^d
	750 ^e	LT	620m 650m 678s 718s
EtMeO(5)	709	RT	613w 642sh 676s ^d
	700	LT	610w 642w 652w 672s ^d
	763 ^e	LT	618m 653s 670s 705s 720s

RT = Room temperature; LT = liquid nitrogen temperature.

- a) Excitation spectra reported for the fluorescence emission peak as shown.
b) Tetraneopentoxypthalocyanine. c) Vibrational satellite of the main ca.710nm peak. d) Excitation peak near 700nm obscured, too close to emitting line. e) Cofacial conformation peak.

Table 3 Relative Emission Intensities of the ca 700nm Emission in Mononuclear and Binuclear Metal-Free Phthalocyanine Species in Toluene/Ethanol (3:2 v/v) at Room Temperature^a

Species	Relative Intensity	Species	Relative Intensity
PcH ₂ ^b	100(8) ^c	Pc-Pc(0)	12(3)
O(1)	17(6.5)	C(2)	11(2.4)
C(4)	33(3)	Cat(4)	24(4)
tBuCat(4)	31(4)	EtMeO(5)	4(.4) ^d ; 24(4.8) ^d

a) The smaller the number, the greater the degree of coupling. Note that scattering prevents an accurate assessment of the liquid nitrogen temperature relative intensities. The data for each species were normalised to the same concentration and corrected for the inner filter effect.³¹ The same excitation frequency was used throughout and assumed to remain at constant exciting intensity. b) Tetraneopentoxypthalocyanine. c) Standard deviation in parentheses. d) Two widely separated chromatographic fractions which must differ significantly in isomer mix.

Table 4 Absorption Electronic Spectroscopic Data for Deprotonated Mononuclear and Binuclear Metal-Free Phthalocyanine Species in Toluene/Ethanol (3:2 v/v)^a

Species	Absorption Spectra (nm)		
	Soret	Soret Half-bandwidth (cm ⁻¹)	(Log ϵ) Q band region
Pc ^{2-b}	352(4.87)	3900	(614)(4.50) (650)w 680(5.12)
Pc-Pc(0)	342(4.93)	6100	(616)w (645)(4.73) 675(4.86) (690)(4.84)
O(1)	340(5.01)	4750	(610)w (644)(4.87) 678(4.92)
C(2)	345(4.49)	6500	640(4.37) 679(4.50)
C(4)	340(4.89)	5800	(616)w 646(4.75) 671(4.84)
Cat(4)	340(5.12)	5050	645(5.12) (670)(4.94) (706)w
tBuCat(4)	338(4.92)	5450	(588)w (612)w 646(4.84) 677(4.81) 710(4.62)
EtMeO(5)	334(4.96)	5650	(590)w 645(4.80) 677(4.77)

a) The deprotonated species were generated in situ, by adding 0.1-0.2ml of 1M tetrabutylammonium hydroxide (in methanol) to a solution of the protonated species (ca 3ml 5×10^{-6} M). br = broad, w = weak; data in parentheses are shoulders. b) Mononuclear.

Table 5 Absorption Electronic Spectroscopic Data for Mononuclear and Binuclear Metal-Free Phthalocyanine Species in the Solid State (Smear)

Species	Absorption Spectra (nm)
---------	-------------------------

PcH ₂ ^a	640, 672, 708
Pc-Pc(0)	662, 690, 713
O(1)	662, 690, 713
C(2)	(620), 654, 680, 713
C(4)	618, 654, 679, 718
Cat(4)	(620), 647, 680, 712
tBuCat(4)	(620), 656, 682, 714
EtMeO(5)	(626), 654, 681, 717

a) Tetraneopentoxypthalocyanine. Shoulders in parenthesis.

Fig.1. The electronic absorption spectra of mononuclear and binuclear neopentoxypthalocyanine species as labelled. A: PCH_2 , B: $Pc-Pc(0)$, $C(0)$, D: $C(2)$, E: $Cat(4)$, F: $t-BuCat(4)$, G: $C(4)$, H: $EtMeO(5)$ RT = room temperature in toluene/ethanol (3:2 v/v); LN_2 = liquid nitrogen cooled species in toluene/ethanol (3:2 v/v); DP = deprotonated species obtained by addition of 0.1ml TBAOH in ethanol to a toluene/ethanol (3ml, 3:2 v/v) solution, at room temperature. To within the volume change error, the DP and RT spectra are to correct relative scale.

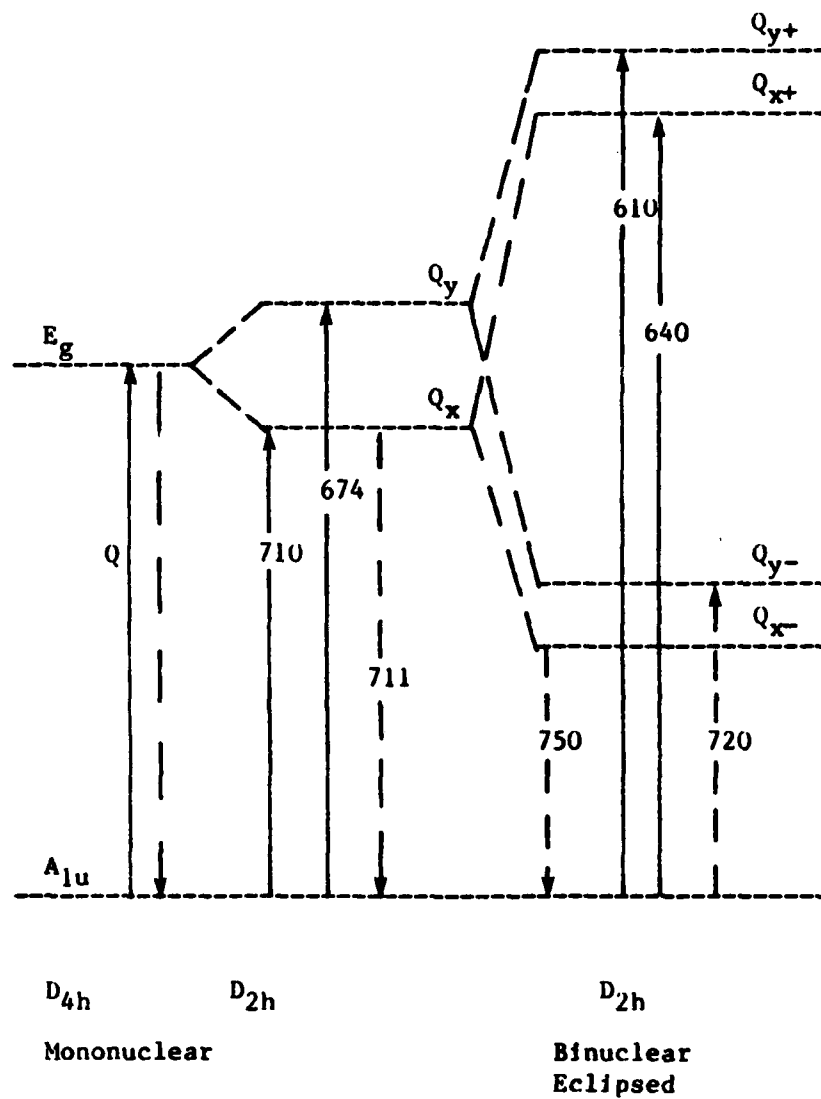
Fig.2. A qualitative orbital energy diagram for exciton coupling. Absorption ———, emission ————. Column 1, a D_{4h} mononuclear metallophthalocyanine species; column 2, a D_{2h} metal-free mononuclear neopentoxypthalocyanine species; column 3, a D_{2h} binuclear eclipsed neopentoxypthalocyanine. Typical wavelengths reported in nm.

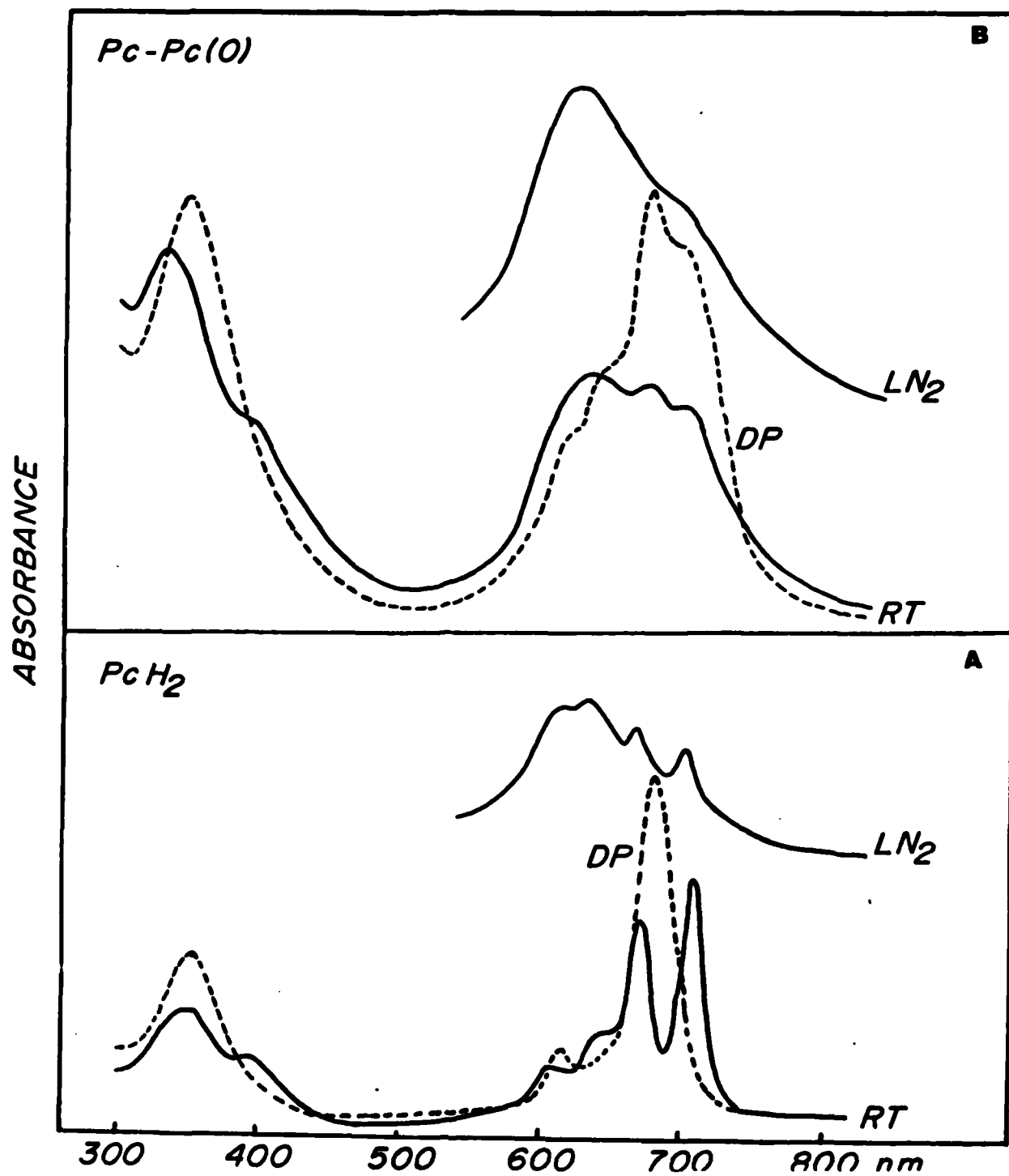
Fig.3 Emission spectra of monuclear and binuclear neopentoxypthalocyanine species in toluene/ethanol (3:2 v/v) solution at room temperature (RT) and at liquid nitrogen temperature (LN_2). Left: Mononuclear neopentoxypthalocyanine. Middle: The $EtMeO(5)$ species at room temperature and liquid nitrogen temperature. Right: Binuclear species as labelled, at liquid nitrogen temperature. All data were collected at approximately the same concentration, per neopentoxypthalocyanine unit, with the same instrument settings. Thus the relative intensities will be approximately correct as illustrated. The labels Q_x , Q_y etc apply to the transitions which we have qualitatively shown coming from the HOMO of the binuclear molecule.

Fig.4 Excitation and related absorption spectra. Left: A, absorption spectrum of mononuclear PcH_2 in toluene/ethanol (3:2 v/v) at room temperature. B, Excitation spectrum of the 778nm vibrational satellite of the EtMeO(5) species at 77 K (uncoupled conformer). Right: C, EtMeO(5) absorption spectrum in toluene/ethanol glass at 77 K. D, Excitation spectrum of the 750 nm emission (excimer) emission of EtMeO(5) in toluene/ethanol at 77 K. E, Same as A.

Fig.5 The solid state crystalline 'smear' and Nujol mull spectra of the labelled mononuclear and binuclear species as shown. The toluene/ethanol room temperature and liquid nitrogen glass spectra are repeated to clearly indicate the shifts in absorption from solution to solid state.

Fig 1





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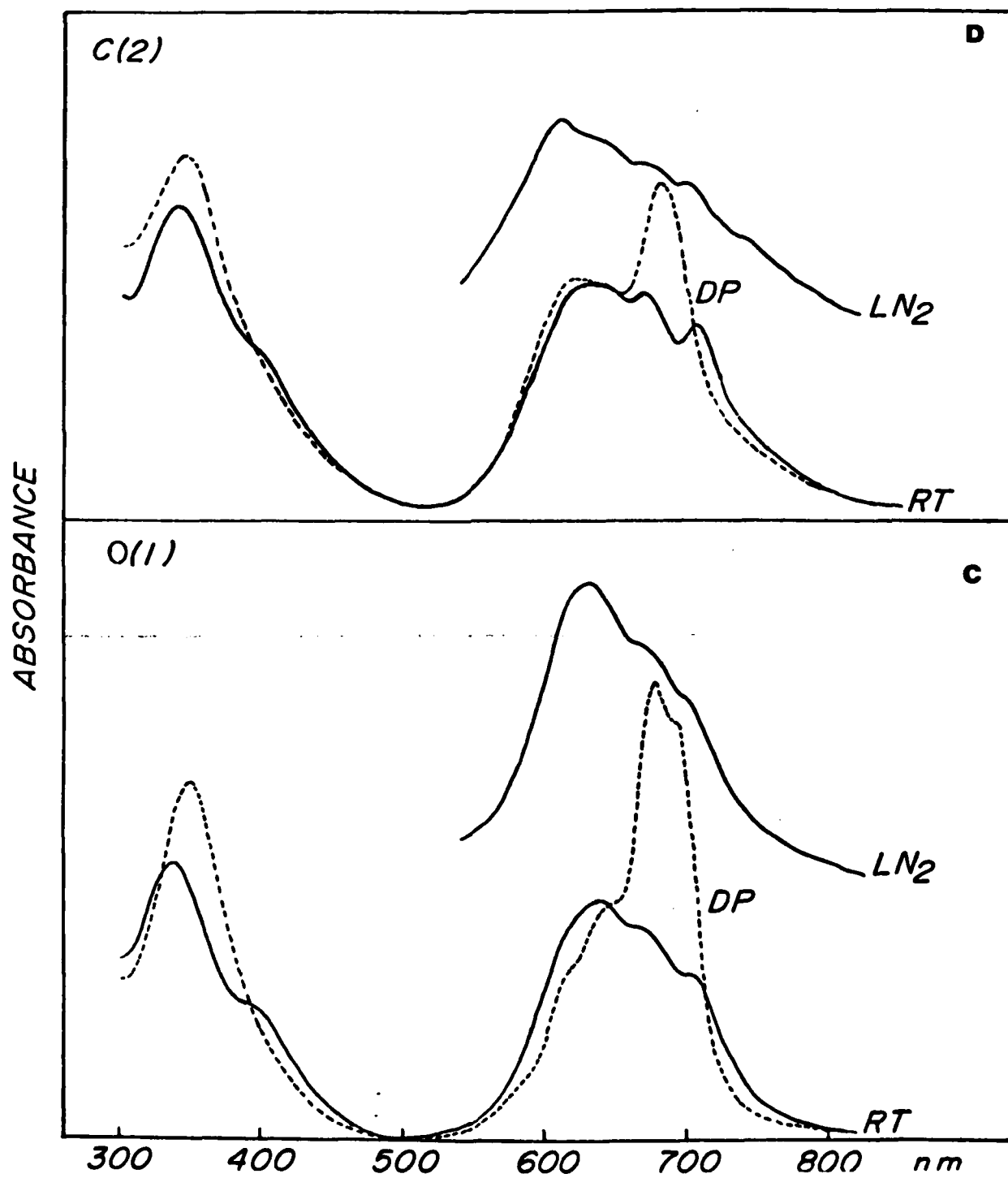


Fig 2

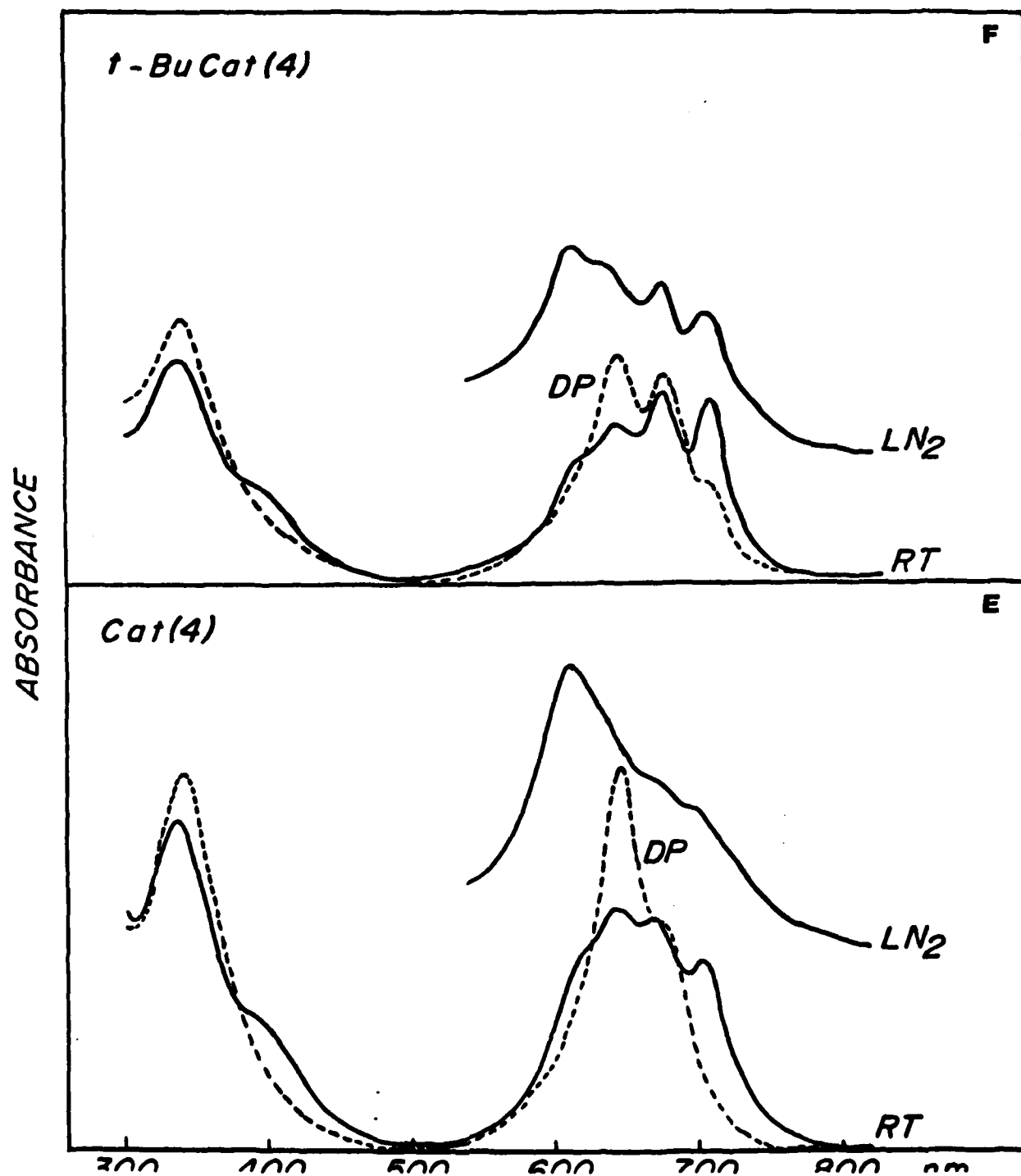


Fig 2

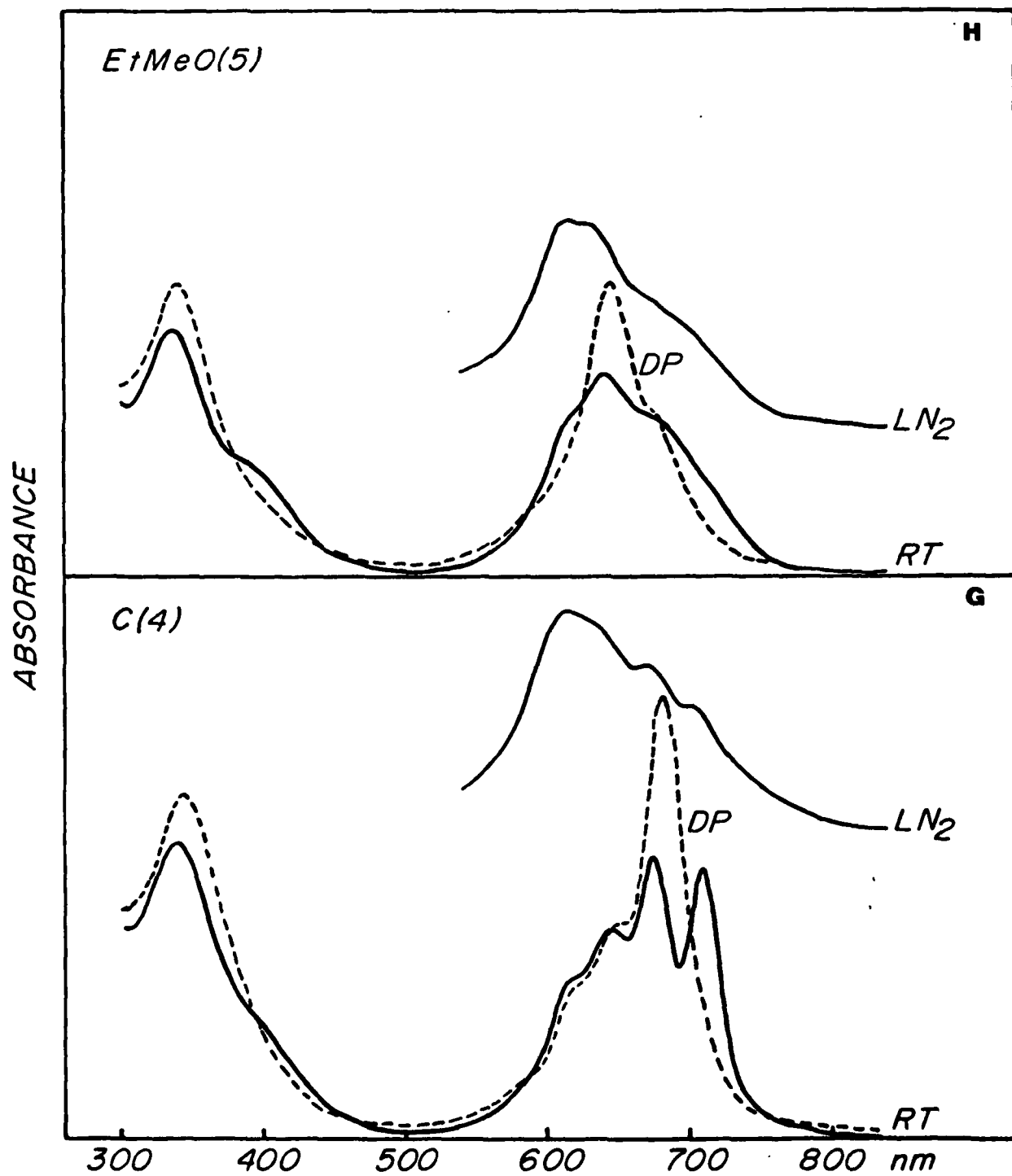
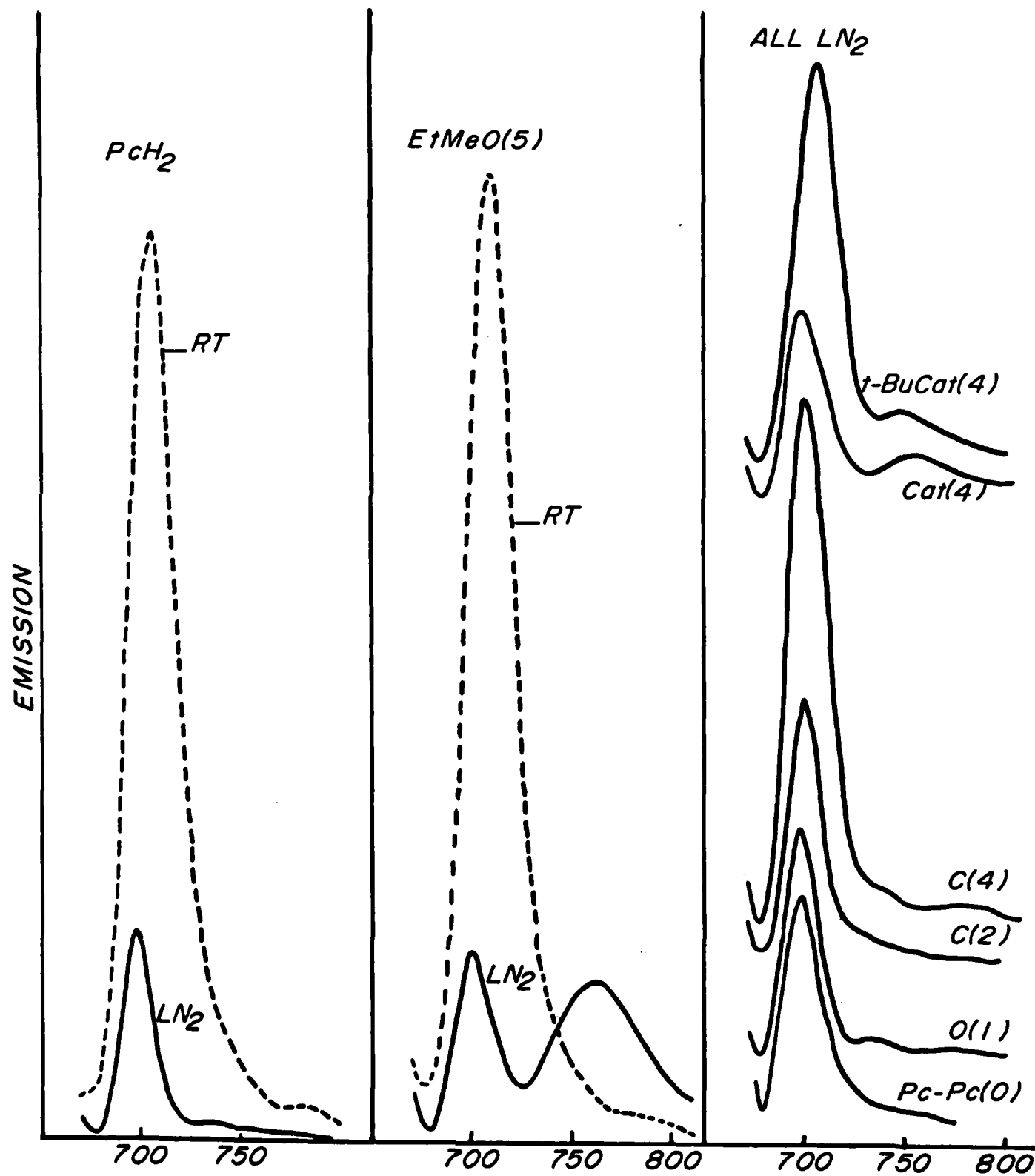
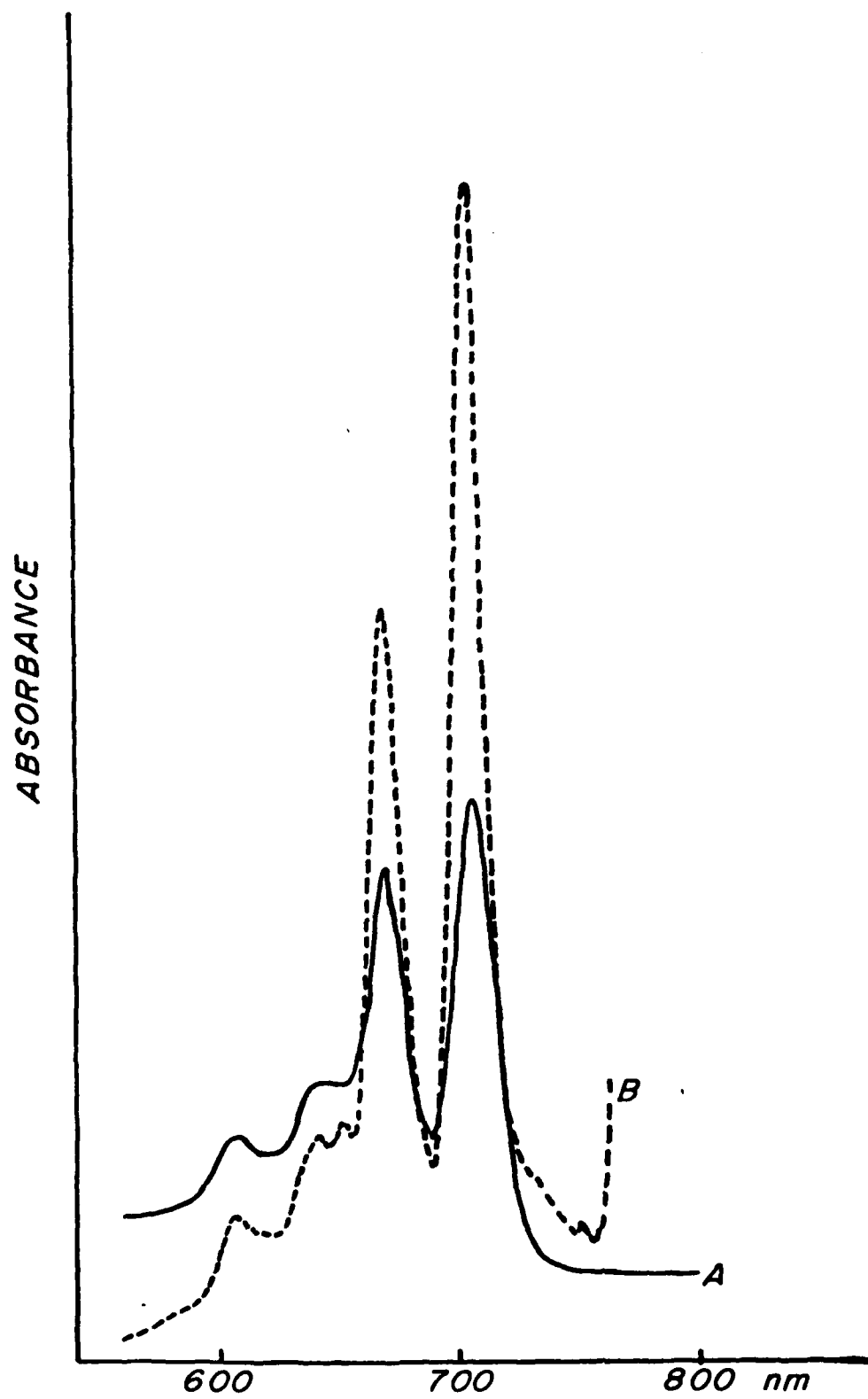


Fig 3



F₁ 4A



F₁, 4 B

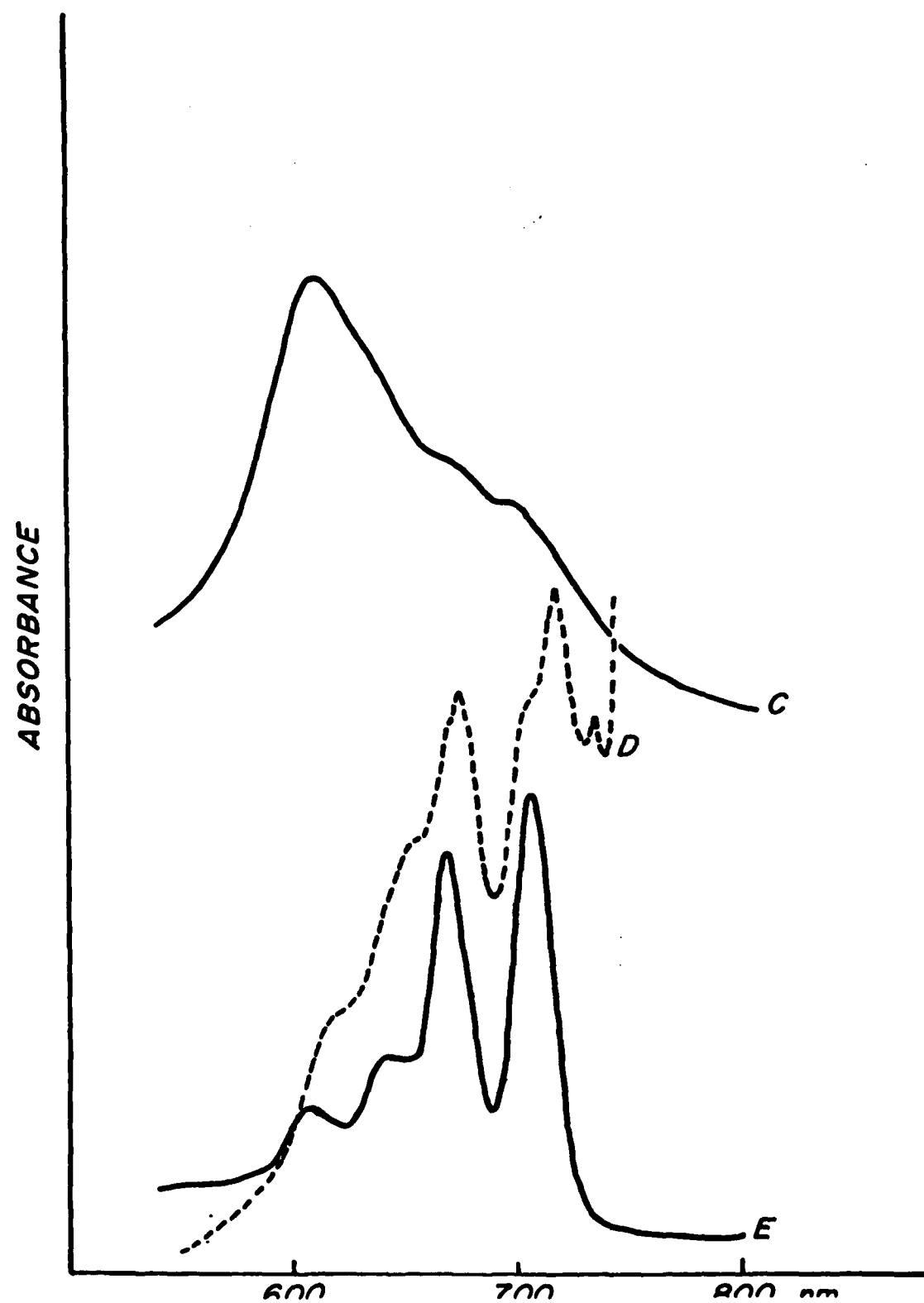


Fig 1

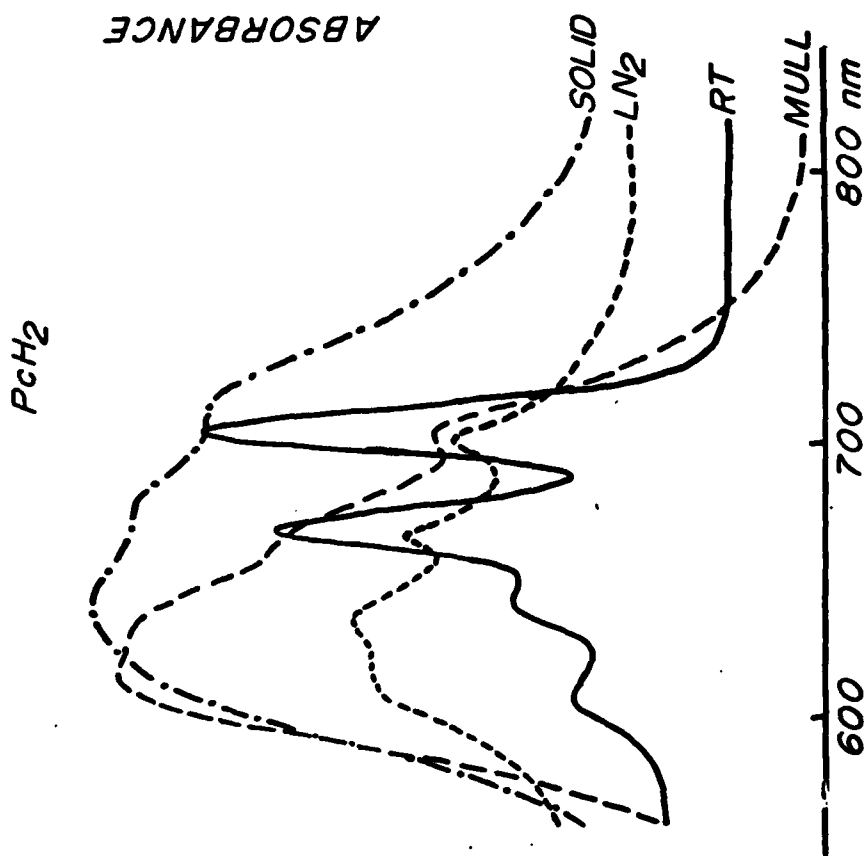
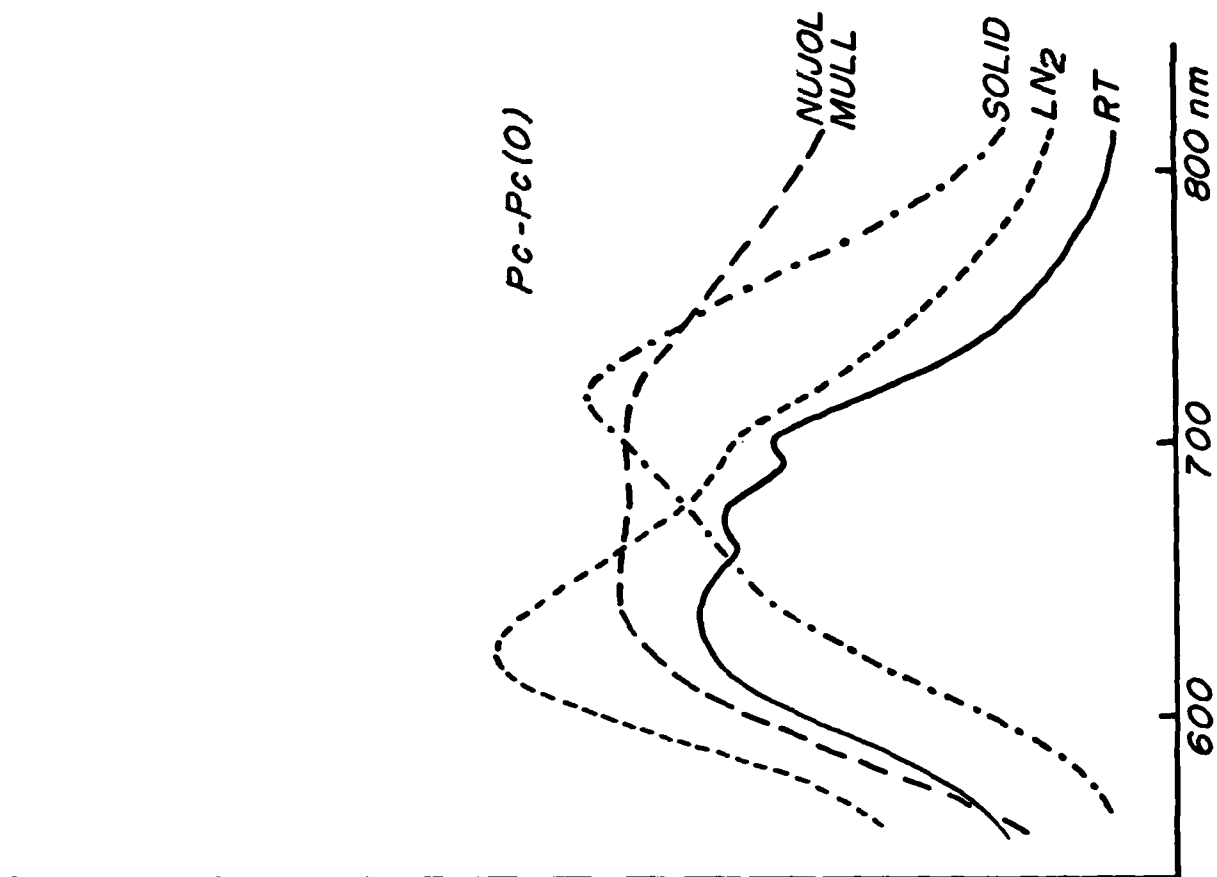
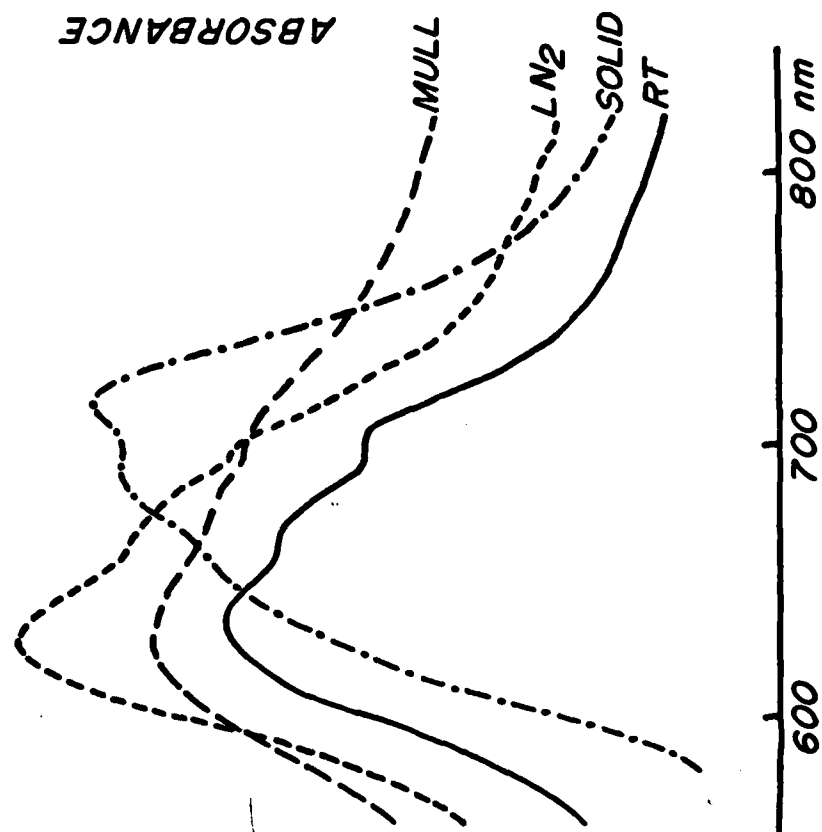
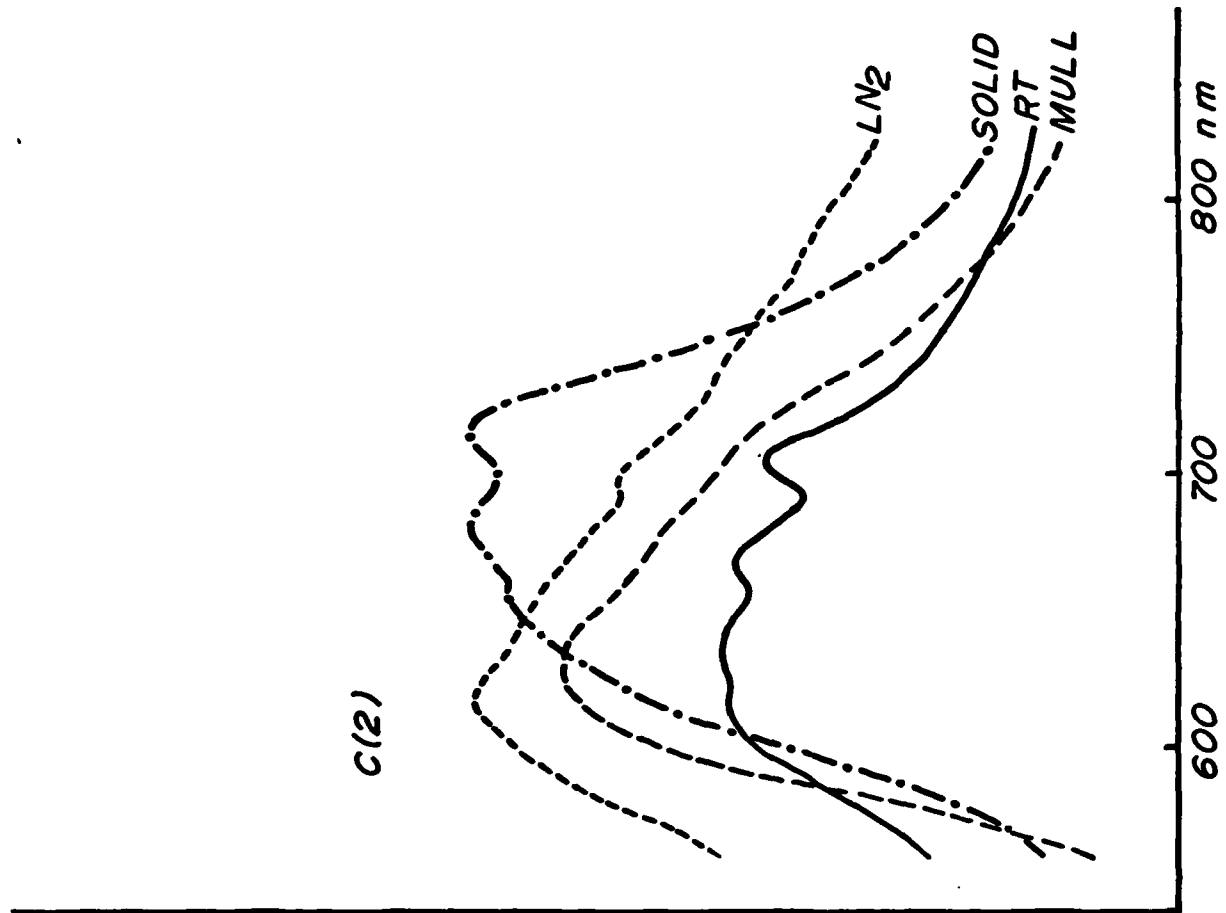


Fig. 5

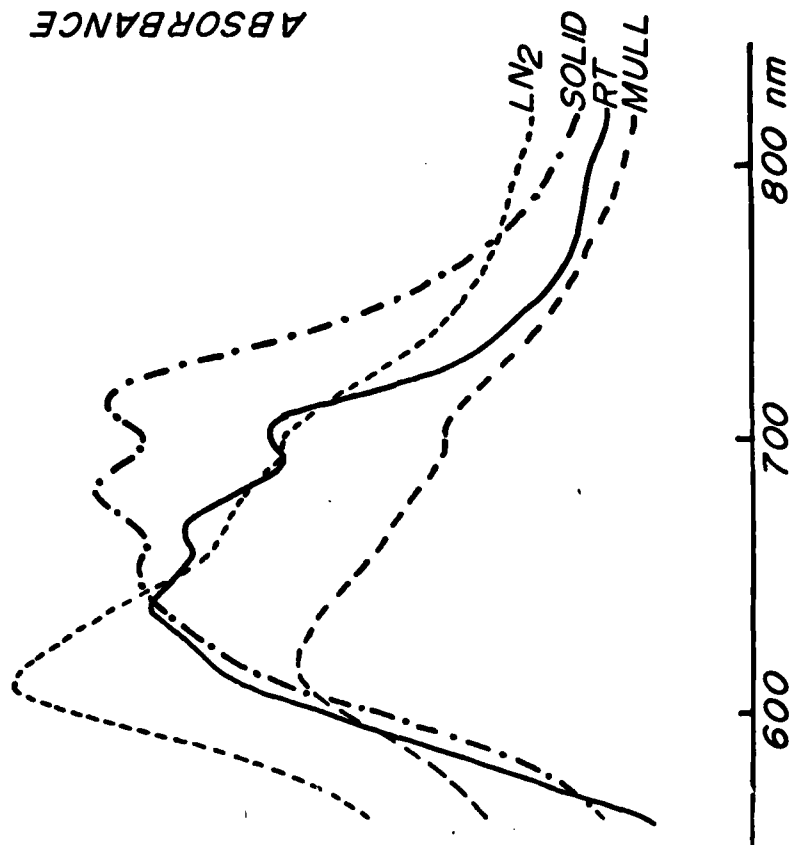
0(1)



0(2)



Cat(4)



t-BuCat(4)

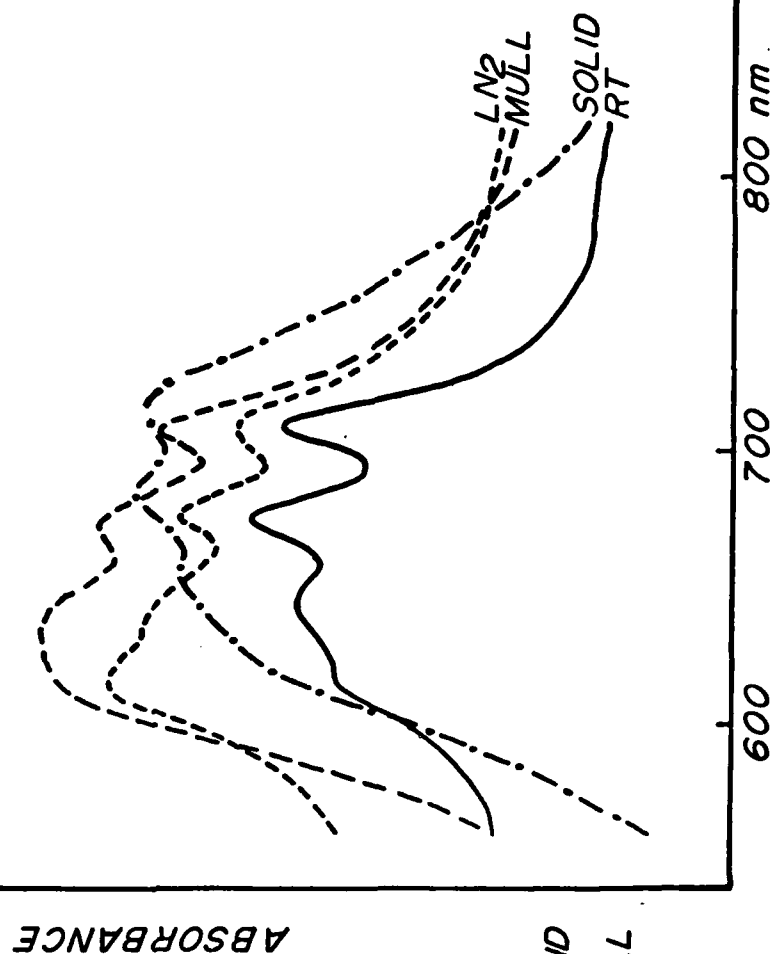
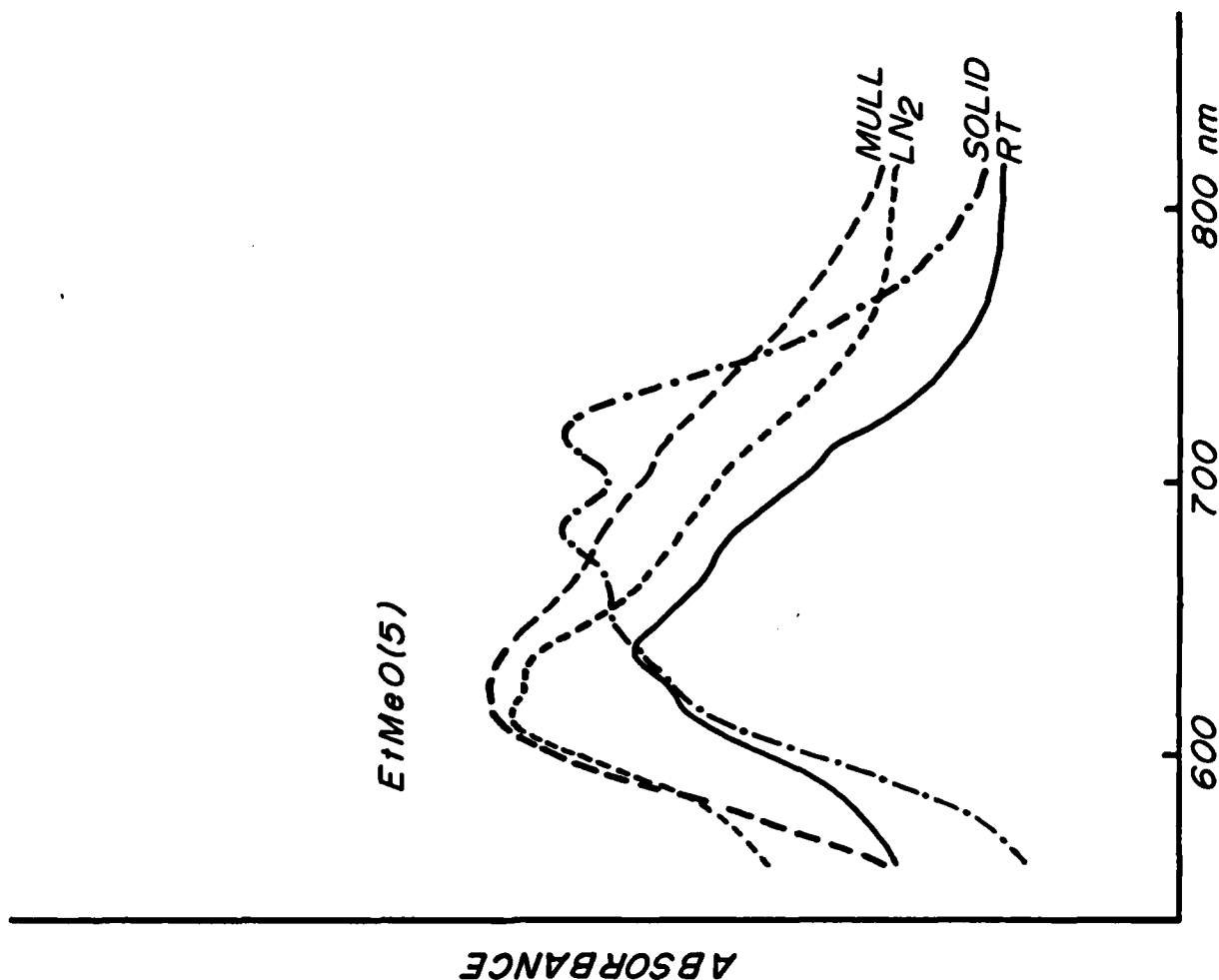
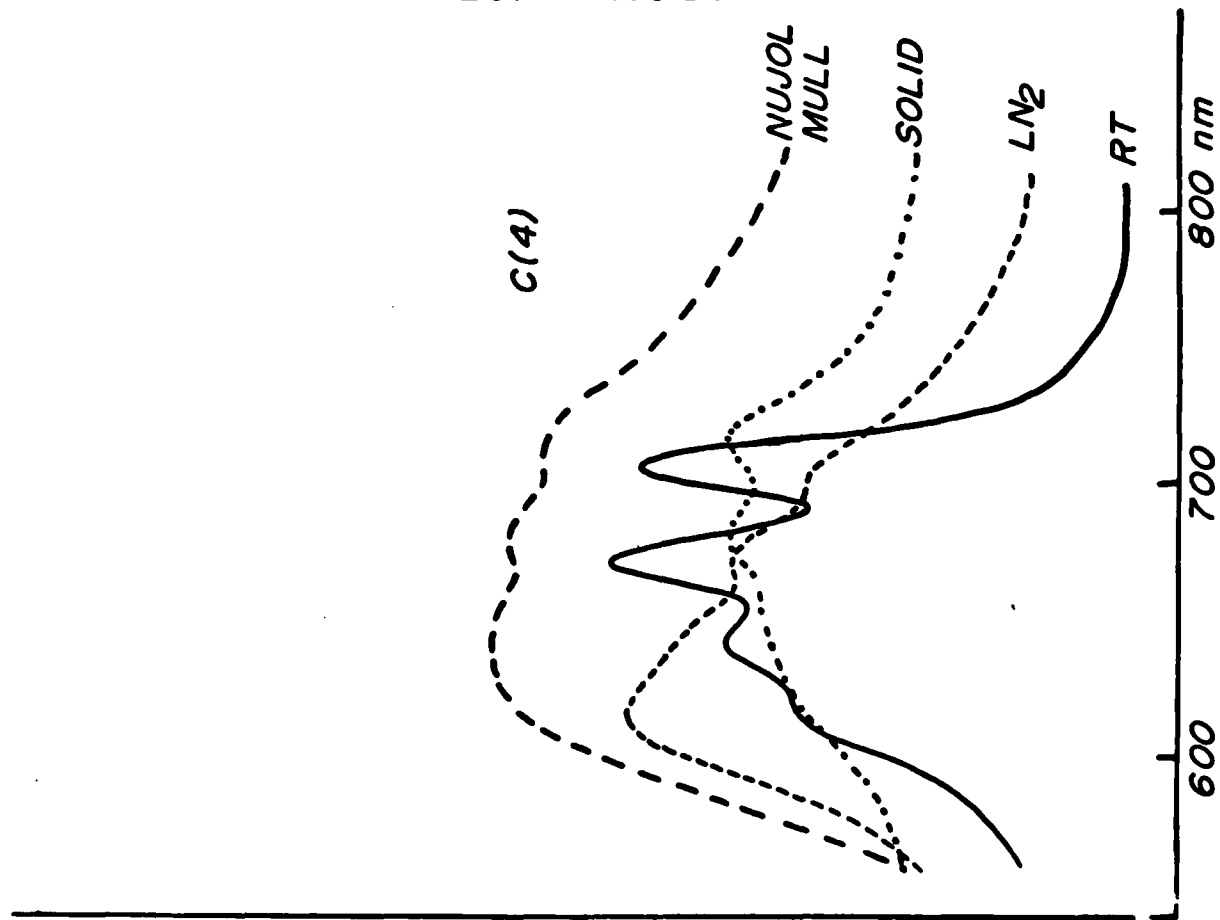


Fig 1



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